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METHOD FOR PRODUCING SALTS OF N-ACYL-N-ALKYLAMINOPROPIONIC ACIDS

[Verfahren zur Herstellung von Salzen von N-Acyl-N-alkylaminopropionsäuren]

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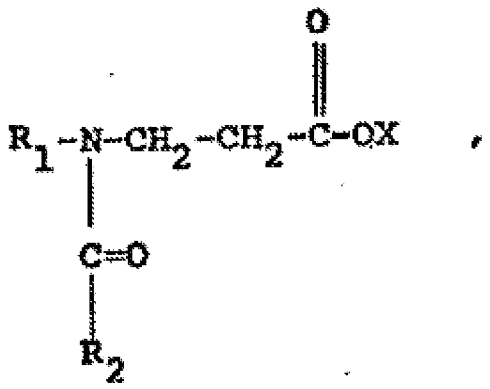
This invention concerns a method for producing salts of N-acyl-N-alkylaminopropionic acids of the general formula



in which

R_1 means a saturated or unsaturated alkyl or alkoxyalkyl residue with 6-22, preferably 12-18, carbon atoms,

R_2 means an alkyl residue with 1-4 carbon atoms, a saturated or unsaturated carboxyalkyl residue with 3-4 carbon atoms, or a carboxyphenyl residue, and

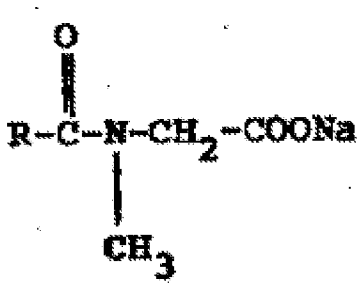
X means an alkali metal or ammonium.

The products produced in accordance with the invention can be used as textile auxiliaries, in particular as finishing agents for textile fibers.

However, they are also suitable as emulsifiers, wetting agents and dyeing auxiliaries and for the production of washing agents and soaps that are gentle to the skin.

The use of salts of N-acylalkylaminoacetic acids, thus similarly structured compounds, as textile /2* auxiliaries is known. For example, in German Patent No. 635 522 compounds of the type

* [Numbers in right margin indicate pagination of the original text.]



(R = long-chain alkyl residue)

and their use as textile auxiliaries are described. These compounds are prepared by acylation of N-methylacetic acid sodium salt (Na sarcosinate) in aqueous phase under the conditions of a Schotten-Baumann reaction after obtaining the sodium sarcosinate from monochloroacetate and methylamine.

This mode of preparation is fraught with significant disadvantages. As is known, in a Schotten-Baumann reaction one has to contend with large losses of the acid chloride, due to which a process conducted on an industrial scale suffers greatly with regard to economy. However, the biggest disadvantage of a Schotten-Baumann reaction conducted on an industrial scale is the necessary formation of more than equivalent amounts of sodium chloride, in addition to considerable amounts of soaps. These undesired products disrupt the process and have to be removed in costly purification operations. In addition, it must be noted that the salts of N-acyl-N-alkylaminoacetic acids, which are obtained in the end in high-loss reactions and with the help of costly purification operations, have an unpleasant, undefinable odor that becomes even stronger after the product has stood for awhile. The odor of these products is found to be troublesome especially when they are used as washing and textile auxiliaries. /3

For this reason there has already been a switch to producing salts of N-acyl-N-alkylaminoacetic acids of the same or analogous type (as described in the above-mentioned German Patent No. 635 522) by

acylating the N-alkylacetic acid sodium salt (alkyl = methyl or ethyl) with the acid anhydrides of higher molecular fatty acids that have 8-22 carbon atoms (German Auslegeschrift Patent Application No. 1 127 359).

Undoubtedly, through this kind of production some of the above-mentioned disadvantages of the prior art are avoided; i.e., less acylation agent is consumed due to uncontrolled side reactions and the end product does not have an unpleasant odor.

However, no teaching is provided for simple removal of the undesirable byproduct that forms in an equivalent amount in the acylation, the long-chain fatty acid.

Extraction with at least twice the amount by weight, with respect to the fatty acid, of inorganic solvents such as ligroin, benzene or ethylene dichloride, and then to separation by decanting, centrifuging, etc., is recommended as a method for separating the molar amount of fatty acid, (see loc. cit., column 6, lines 35-55). There may be a genuine need to avoid such costly and lengthy operations in industrial processes

It was found that salts of N-acyl-N-alkylaminopropionic acids of the formula

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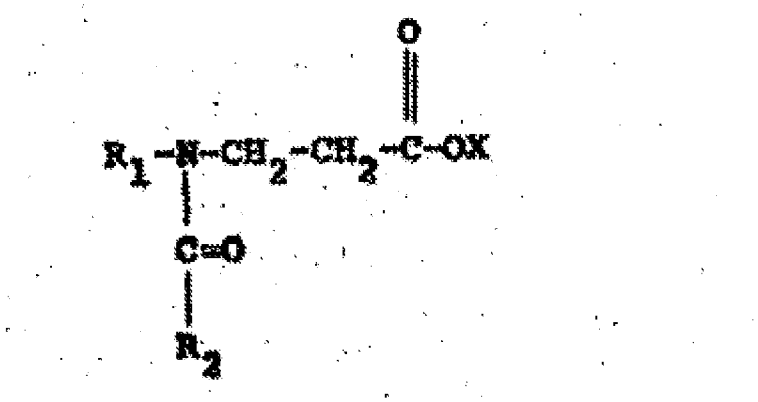


with long-chain alkyl and short-chain acyl residues, which exhibit similar structure and analogous efficiency to textile auxiliaries as do the salts of the above-mentioned N-acyl-N-alkylaminoacetic acids, can be produced in a very simple way if alkylamines of the formula R_1-NH_2 are added to acrylonitrile,

acrylic acid esters or acrylic acid amide, the resulting N-alkylaminopropionic acid derivatives are reacted with anhydrides of lower molecular carboxylic acids, and the resulting N-acyl-N-alkylaminopropionic acid derivatives are treated with alkaline agents at 60-120°C, preferably 80-100°C.

The reaction of the N-alkylaminopropionic acid derivatives obtained in the first step can be undertaken with anhydrides of fatty acids containing 2-5 carbon atoms, with anhydrides of saturated or unsaturated dicarboxylic acids having 4-5 carbon atoms, or with phthalic anhydride. Acetanhydride is especially suitable for this reaction.

N-Alkylaminopropionic acid esters that arise in the first step through addition of the above-mentioned monoalkylamines to acrylic acid esters are especially suitable as N-alkylaminopropionic acid derivatives for this reaction. As the alkaline agents for treatment of the N-acyl-N-alkylaminopropionic acid derivatives obtained in the second step, one uses aqueous alkalis that contain 2-50 wt%, preferably 5-25 wt%, alkali hydroxide, or ammonia water that contains 2-35 wt%, preferably 5-25 wt%, ammonium hydroxide.

The treatment of the N-acyl-N-alkylaminopropionic acid derivatives is especially advantageously /5 carried out in the presence of 3-5 wt% lower alcohols with respect to the starting product.

The addition of the primary alkylamines of the formula R_1-NH_2 to acrylic acid derivatives such as acrylic acid esters, acrylonitrile or acrylamide is carried out in a known way (see U.S. Patent Nos. 2 816 911 and 3 467 707, German Patent No. 598 185). One advantageously reacts molar amounts of alkylamine and an acrylic acid compound, namely in the presence of small amounts (about 1% with respect to the mixture of amine and acrylic derivatives) of concentrated acetic acid, at temperatures from 80-90°C. To accelerate the addition it is advisable to conduct the addition in the presence of small

amounts of lower alcohols, for example ethyl alcohol or isopropyl alcohol (about 3-5% with respect to the reaction mixture).

As alkylamines of formula R_1-NH_2, one can use saturated or unsaturated primary amines with 6-22, preferably 12-18, carbon atoms. Examples are: n-hexylamine, n-heptylamine, n-octylamine, n-nonylamine, n-decylamine, n-undecylamine, n-dodecylamine, n-tridecylamine, n-tetradecylamine, n-pentadecylamine, n-hexadecylamine, n-heptadecylamine, n-octadecylamine, n-nonadecylamine, n-eicosylamine, n-heneicosylamine, n-docosylamine, propoxypropylamine, butoxypropylamine, hexoxypropylamine, n-octyloxypropylamine, decyloxypropylamine, dodecyloxypropylamine, tetradecyloxypropylamine, hexadecyloxypropylamine, octadecyloxypropylamine, oleylamine, oleyloxypropylamine. One can use as acrylic acid esters: methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate; however, preference should be given to inexpensive commercial products like ethyl acrylate and methyl acrylate.

The reaction of the N-alkylaminopropionic acid derivatives with anhydrides of lower carboxylic /6
acids, an acylation reaction, is carried out with 1-1.2 mol, preferably 1.05-1.1 mol, anhydride per mol of N-alkylaminopropionic acid derivative, at 40-100°C, preferably 50-80°C. At a reaction temperature of about 70°C the acylation is generally complete after about 1 h. Care should be taken that after the acylation the reaction mixture contains less than 0.2% basic nitrogen.

Possibilities as anhydrides of lower carboxylic acids, which are used for acylation of the N-alkylaminopropionic acid derivatives obtained in the first step are: acetic anhydride, propionic anhydride, butyric anhydride, valeric anhydride, isovaleric anhydride, maleic anhydride, succinic anhydride, glutaric anhydride, phthalic anhydride.

The relevant anhydrides are readily available commercial products or technically easily accessible compounds.

The mixture of N-acyl-N-alkylaminopropionic acid derivative, equivalent amounts of monocarboxylic acid and small amounts of unreacted carboxylic anhydride obtained after acylation with monocarboxylic acid anhydrides can be separated from the byproducts in a very simple way.

The monocarboxylic acid, which is formed in an equivalent amount, is low-molecular and therefore both water-soluble and easily distillable; thus there are two possibilities for removing it with extraordinarily low material, time and technical cost: one dissolves the acid out with water, where the residues of the anhydride hydrolyze and are removed in a simple process step; or the low-boiling low-molecular carboxylic acid, including the residues of the anhydride, are distilled out ("skimmed off"). /7

Both operations can be carried out extraordinarily easily, quickly and completely.

The product obtained after the acylation with dicarboxylic anhydrides contains only small amounts of unreacted anhydride as byproduct. Since these products do not have significant negative effects on the properties of the products produced in accordance with the invention, it is not necessary to separate them.

The saponification of the N-acyl-N-alkylaminopropionic acid derivatives that come from the acylation with monocarboxylic acid anhydrides is carried out by heating with 1-1.2 mol, preferably 1.05-1.1 mol, aqueous alkalis. In the saponification of the corresponding products that result from the acylation with dicarboxylic acid anhydrides, twice the amount of alkali is required. In the saponification of the N-acyl-N-alkylaminopropionic acid esters, saponification with ammonia water is also possible. The ammonium salts form.

Saponification is carried out at 60-120°C, preferably 80-100°C. In many cases the saponification rate is greatly increased through the presence of small amounts of lower alcohols. Ethanol and isopropanol were especially suitable. Amounts of 3-5 wt% with respect to the starting product are used. Such small

amounts of lower alcohols in general do not have any effect on the technical application properties of the end products, and as such can remain in the reaction product.

(For some applications it can be advantageous to produce alkaline earth salts or N-alkylammonium /8
salts from the resulting alkali salts. This is managed in a known way by reacting the free N-acyl-N-alkylaminopropionic acids with amines or the oxides, hydroxides or carbonates of the alkaline earths in the form of aqueous slurries. The free N-acyl-N-alkylaminopropionic acids that are necessary for this reaction are obtained from their aqueous alkali salt solutions, from which they are precipitated by acidification with aqueous mineral acids.)

The alkali salts of N-acyl-N-alkylaminopropionic acids that are obtained are suitable as textile auxiliaries in a manner similar to those in the above-mentioned German Patent No. 635 522 and the N-acyl-N-alkylaminoacetic acids described in the Auslegeschrift Patent Application No. 1 127 359.

However, they are produced in a very much simpler and more economical way, since the acylation is carried out in a nonaqueous medium and consequently without losses of acylation agent and, in addition, the mol of carboxylic acid that forms in the acylation can be removed by simple distillation or by washing with water. Surprisingly, the N-acyl group introduced previously by acylation remains in the subsequent saponification of the nitrile, amide or ester group. The long hydrophobic alkyl residue R_1 that is needed for the activity of this type of compound is, in the method in accordance with the invention, introduced in the first step through an addition reaction in which no byproducts are formed. Costly removal of large amounts of higher-molecular fatty acids by dissolving them out with at least twice the amount of organic solvents, as is necessary according to the prior art, is thus avoided in accordance with the invention.

Example 1 /9

966 g (3 mol) of an addition product of molar amounts of stearylamine and acrylonitrile is acylated, while stirring, with 322 g (3.15 mol) acetic anhydride. The exothermic reaction is controlled through an appropriate dropping rate of the acetic anhydride so that the reaction takes place in a temperature range between 50 and 70°C. After the end of the addition, the reaction mixture is heated to 70°C until the content of basic nitrogen is less than 0.2%. Then the free acetic acid is washed with hot water, and at the same time the low basic fractions in the form of the acetic acid salt are removed. To eliminate the remaining acetic acid, washing is carried out with 2-5% sodium hydroxide solution. After dehydration one obtains 1052 g (96.5% of theory) N-acetylstearylaminopropionitrile.

Calculated: N: 7.67%

Found: N: 7.7%

Base N: 0.1%

The addition product of stearylamine and acrylonitrile is prepared as follows: A mixture of 269 g (1 mol) stearylamine, 55.6 g (1.05 mol) acrylonitrile, 16.0 g isopropanol and 6.1 g acetic anhydride (concentrated) is held at a temperature of 80-90°C for 3 h while stirring. Noticeable positive heat of reaction is seen at the beginning of the reaction. After the reaction time noted above, conversion is practically 100%. The reaction product consists of over 95% stearylaminopropionitrile.

For saponification 182 g (0.5 mol) N-acetyl-N-stearylaminopropionitrile is mixed with 114 g /10 isopropanol and heated to reflux in a stirred vessel that is equipped with a thermometer, a dropping funnel and reflux condenser. While stirring 88 g 25% (0.55 mol) sodium hydroxide solution and 19 mL water are slowly added by drops. The dropping rate is regulated so that only slight cloudiness develops. The saponification is stopped when development of ammonia can no longer be detected. The resulting 50% aqueous-alcohol solution of the sodium salt of N-acetylstearylaminopropionic acid has a paste-like

consistency at room temperature. The resulting colorless to pale yellow product gives a clear solution when dissolved in water.

Example 2

1101 g (3 mol) of the addition product of molar amounts of oleylamine and ethyl acrylate is acetylated with 322 g (3.15 mol) acetic anhydride under the conditions given in Example 1. After washing with water, dilute sodium hydroxide solution, and drying, 1178 g (96% of theory) N-acetyloleylaminopropionic acid ethyl ester was obtained as a slightly colored paste.

Calculated:	N: 3.42%
Found:	N: 3.45%
Base	N: 0.15%

The addition product of oleylamine and ethyl acrylate is obtained from stearylamine and acrylonitrile /11 under the same conditions as the addition product described in Example 1. The colorless or only slightly colored reaction product is more than 95% alkylaminopropionic acid ethyl ester.

For saponification, 409 g (1.0 mol) N-acetyloleylaminopropionic acid ethyl ester, 84 g 50% (1.05 mol) sodium hydroxide solution and 314 g distilled water are mixed together. The reaction mixture is heated to 80°C while stirring. After about 10-15 min there is a significant increase of viscosity, which makes it necessary to switch the agitator off. The reaction mixture is heated for another 2 h at the temperature noted above, so that the saponification is carried out to completion. The resulting aqueous-alcohol, approximately 50% solution of N-acetyloleylaminopropionate sodium salt solidifies at room temperature to a colorless paste, which forms a clear solution when dissolved in water.

Example 3

768 g (3 mol) of the addition product of molar amounts of laurylamine and acrylamide are acetylated with 322 g (3.15 mol) acetic anhydride under the conditions given in Example 1. After washing and drying the product, 823 g (92% of theory) N-acetyllaurylaminopropionic amide is obtained.

Calculated: N: 9.39%

Found: N: 9.45%

Base N: 0.2%

The addition product of laurylamine and acrylamide is obtained by heating 555 g (3 mol) laurylamine, 234 g (3.3 mol) acrylamide, 40 g isopropanol and 10 g acetic acid (concentrated) to a /12 temperature of 80-90°C for 8 h.

Saponification of the N-acetyllaurylaminopropionic acid amide under the conditions given in Example 1 produces the sodium salt of N-acetyllaurylaminopropionic acid, which still contains small amounts (about 1-2 wt%) of the sodium salt of laurylaminodipropionic acid. The reaction mixture is a colorless to slightly colored paste, which produces a clear solution when dissolved in water.

Example 4

98 g (1.0 mol) maleic anhydride is added to 369 g (1 mol) of the addition product of molar amounts of stearylamine and ethyl acrylate (prepared as in Example 2) over a period of 30 min, while heating to 60°C and stirring. After the exothermic reaction diminishes, the reaction product is heated for another hour at 80°C. After washing with water, dilute acetic acid, and drying, 435 g (93% of theory) N-maleinylstearylaminopropionic acid ethyl ester is obtained. The slightly yellow ester has a waxy consistency at room temperature.

Calculated: N: 3.0%

Found: N: 3.02%

Base N: 0.1%

A mixture of 233.5 g (0.5 mol) N-maleinylstearylaminopropionic acid ethyl ester, 75 mL 25% (1.1 mol) ammonia water and 162.5 g distilled water are heated to 80°C for 4 h while stirring. The progress of the saponification can be observed from the increase of viscosity. After cooling, the /13
approximately 50% aqueous-alcohol solution of the diammonium salt of N-maleinylstearylaminopropionic acid solidifies to a clear gel-like paste. The saponification product dissolves in water, forming a clear solution, and has a pH value of about 9. It can be adjusted to the desired pH value with salt or acetic acid.

Example 5

322 g (3.15 mol) acetic anhydride is added dropwise while stirring to 1029 g (3 mol) of the addition product of molar amounts of lauryloxypropylamine and ethyl acrylate. The reaction and the processing take place as described in Example 1. The yield of washed and dried N-acetyl-N-lauryloxypropylaminopropionic acid ethyl ester is 1295 g (97.0% of theory).

Calculated, total: N: 4.08%

Found, total: N: 4.02%

Base N: 0.15%

The addition product of lauryloxypropylamine and ethyl acrylate is obtained under the same conditions as indicated for the preparation of the addition product of stearylamine and acrylonitrile given in Example 1.

Preparation of the sodium salt of N-acetyl-N-lauryloxypropylaminopropionic acid takes place by saponification of 386 g (1 mol) of the ethyl ester of this compound with 84 g (1.05 mol) sodium

hydroxide solution (50 wt%) and 296 g distilled water. The saponification conditions correspond to those given in Example 2. The resulting 50% saponification product forms a paste at room /14
temperature and forms a clear solution when dissolved in water.

Example 6

570 g (2 mol) of the addition product of molar amounts of laurylamine and ethyl acrylate are reacted with 332 g (2.1 mol) butyric anhydride under the acylation conditions given in Example 1, while stirring. Then the butyric acid, which formed in an equivalent amount, was distilled out at reduced pressure (15-20 m/m [sic]). The maximum reboiler temperature is in this case 130°C. Yield: 695 g (97.8% of theory) N-butyryl-N-laurylaminopropionic acid ethyl ester.

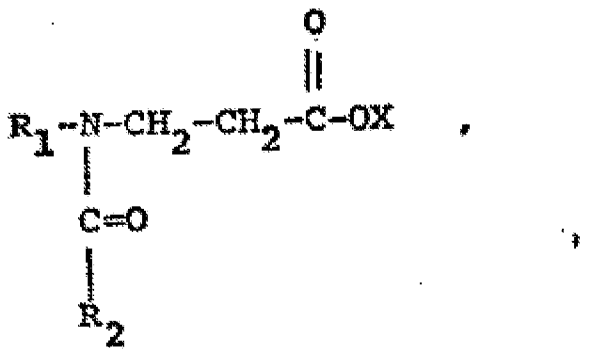
Calculated, total:	N: 3.95%	
Found, total:	N: 3.89%	
Base	N: 0.2%	Acid number: 1.4

The addition product of laurylamine and ethyl acrylate is obtained under the reaction conditions given in Example 1, as employed for the preparation of the addition product of stearylamine and acrylonitrile.

The sodium salt is obtained by saponification of 355 g (1 mol) N-butyryl-N-laurylaminopropionic acid ethyl ester with 84 g 50 wt% sodium hydroxide solution (1.05 mol) and 270 g distilled water under the saponification conditions in Example 2. The approximately 50% Na salt of N-butyryl-N-laurylaminopropionic acid that is in the form of a paste at room temperature dissolves in water to form a clear solution.

Claims /15

1. A method for producing salts of N-acyl-N-alkylaminopropionic acids of the general formula



in which R_1 means a saturated or unsaturated alkyl residue or alkoxyalkyl residue with 6-22, preferably 12-18, carbon atoms, R_2 means an alkyl residue with 1-4 carbon atoms, a saturated or unsaturated carboxyalkyl residue with 3-4 carbon atoms or a carboxyphenyl residue, and X means an alkali metal or ammonium, characterized by the fact that alkylamines of the formula R_1-NH_2 are added in a substantially known way to acrylonitrile, acrylic acid esters or acrylamide, the resulting N-alkylaminopropionic acid derivatives are reacted with anhydrides of lower molecular carboxylic acids, and the resulting N-acyl-N-alkylaminopropionic acid derivatives are treated with alkaline agents at 60-120°C, preferably 80-100°C.

2. A method as in Claim 1, characterized by the fact that the N-alkylaminopropionic acid derivatives obtained in the first step are reacted with anhydrides of fatty acids that contain 2-5 carbon atoms.

3. A method as in Claim 1, characterized by the fact that the N-alkylaminopropionic acid derivatives /16 obtained in the first step are reacted with acetanhydride.

4. A method as in Claim 1, characterized by the fact that the N-alkylaminopropionic acid derivatives obtained in the first step are reacted with anhydrides of saturated or unsaturated dicarboxylic acids that contain 4-5 carbon atoms.

5. A method as in Claim 1, characterized by the fact that the N-alkylaminopropionic acid derivatives obtained in the first step are reacted with phthalic anhydride.

6. A method as in Claim 1, characterized by the fact that in the first step the alkylamines are added to acrylic acid esters and the resulting N-alkylaminopropionic acid esters are reacted with acetanhydride.

7. A method as in Claims 1-6, characterized by the fact that the N-acyl-N-alkylaminopropionic acid derivatives obtained in the second step are treated with 2-50, preferably 5-25 wt% alkali hydroxide solution, or 2-35, preferably 5-35 wt% aqueous ammonia.

8. A method as in Claim 7, characterized by the fact that the process is carried out in the presence of 3-5 wt% lower alcohols, with respect to the starting product.